



Short communication

Effect of CO and oxygen on anode degradation in polymer electrolyte fuel cell



Yoji Nakamori^{a,b,*}, Naotoshi Suzuki^a, Kazuhisa Tanaka^a, Tsutomu Aoki^a,
Toshiyuki Nohira^b, Rika Hagiwara^b

^a Toshiba Fuel Cell Power Systems Corporation, 4-1, Ukishima-cho, Kawasaki-ku, Kawasaki-shi, Kanagawa 210-0862, Japan

^b Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto-shi, Kyoto 606-8501, Japan

H I G H L I G H T S

- The CO tolerance of PEFC anode was evaluated by hydrogen pump with supplying CO.
- The CO tolerance was deteriorated by the combination of CO and O₂.
- Decomposition of ionomer was caused by H₂O₂ as a by-product of ORR.
- Decomposition of the ionomer was accelerated by CO.
- The CO tolerance is speculated to be caused by the decomposition of the ionomer.

A R T I C L E I N F O

Article history:

Received 22 January 2013

Received in revised form

2 May 2013

Accepted 8 May 2013

Available online 18 May 2013

Keywords:

Polymer electrolyte fuel cell

CO tolerance

Ionomer

Degradation factor

A B S T R A C T

CO tolerance of a polymer electrolyte fuel cell was measured before and after accelerated degradation cell operation in which hydrogen with 200, 500, 1000, and 1500 ppm of CO was supplied to the anode and air was supplied to the cathode in the open-circuit condition. The decrease in CO tolerance was more pronounced when the concentration of CO was increased. However, CO tolerance did not decrease when nitrogen, instead of air, was supplied to the cathode. The amount of fluoride ion in the drain water during the cell operation increased when hydrogen containing 500 ppm CO was supplied to the anode, which indicates the decomposition of perfluorocarbon ionomer. It was found that the combination of CO and oxygen deteriorated the ionomer because H₂O₂ that was produced as a by-product of the oxygen reduction reaction cannot be completely reduced to water. This is due to the decreased surface area of the Pt–Ru alloy catalyst because of CO adsorption, which results in the degradation of the CO tolerance.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are now being developed for commercial worldwide production. PEFCs generate electrical power and heat by the hydrogen oxidation reaction (HOR) at the anode and the oxygen reduction reaction (ORR) at the cathode. PEFCs are targeted for use as cogeneration systems for houses and buildings. However, a significant improvement in durability is required before PEFCs can be reliably used worldwide [1]. For residential PEFC systems, hydrocarbon gas such as town gas is often

used as a source of hydrogen. Hydrocarbon gas is reformed to produce a gas mixture containing hydrogen, carbon dioxide, and a trace amount of carbon monoxide (CO) before being supplied to the anode. However, CO in the reformed gas is known to suppress the HOR on the platinum catalyst because it adsorbs on the platinum surface [2–4]. Therefore, platinum–ruthenium alloy on carbon black (Pt–Ru/C) is used as the anode catalyst for residential PEFCs to mitigate the effect of CO adsorption [5–7]. The CO-tolerance of Pt–Ru/C is reported to decay by potential cycling [8]. It is believed that a decrease in CO tolerance of Pt–Ru/C should not occur as long as the potential is kept near the H⁺/H₂ potential in practical operation. Nevertheless, a reduction in CO tolerance is actually observed in long-term operation, the cause of which is still unknown.

* Corresponding author. Tel.: +81 44 288 8021; fax: +81 44 288 8212.

E-mail address: yoji.nakamori@glb.toshiba.co.jp (Y. Nakamori).

In this study, the effects of CO and oxygen on the anode degradation in PEFCs were investigated by evaluating the CO tolerance. Furthermore, the degradation of the ionomer made of fluorocarbon was evaluated by measuring the fluoride ion content in the drain water of the cell.

2. Experimental

2.1. CO tolerance measurement

A subscale test cell having 25 cm² of electrode area was used to evaluate the CO tolerance of an anode in a membrane electrode assembly (MEA). Both the anode and cathode were composed of catalyst layers and gas-diffusion layers. The anode catalyst layer consisted of Pt–Ru/C catalyst (TEC62E58, Tanaka Kikinzoku Kogyo K.K.) and perfluorocarbon ionomer (Nafion D520, DuPont), while the cathode catalyst layer consisted of Pt/C catalyst and perfluorocarbon ionomer. The gas-diffusion layers for both the electrodes were composed of carbon black and polytetrafluoroethylene (PTFE) pasted on carbon papers. A perfluorocarbon polymer membrane with thickness of 30 μm was used as an electrolyte.

Fig. 1 shows a schematic diagram of the test cell to evaluate CO tolerance of the anode. All the tests were performed at 70 °C and under full humidification. First, the voltage between the anode and cathode in the hydrogen pump operation was measured at current densities of 0 to 500 mA cm^{−2} when pure hydrogen gas was supplied to both the anode and cathode. HOR occurs on the Pt–Ru/C catalyst in the anode (Eq. (1)) and a proton reduction reaction occurs on the Pt/C catalyst in the cathode (Eq. (2)). The cell voltage ($V(\text{H}_2)$) comprises the overpotential of HOR ($\eta_a(\text{H}_2)$), the overpotential of the proton reduction reaction ($\eta_c(\text{H}^+)$), and an ohmic loss (IR) in the membrane (Eq. (3)).



$$V(\text{H}_2) = \eta_a(\text{H}_2) + \eta_c(\text{H}^+) + IR \quad (3)$$

Subsequently, hydrogen containing 200 ppm of CO was supplied to the anode, and pure hydrogen was supplied to the cathode in the open-circuit condition for 3 h. Then, the cell voltage ($V(\text{H}_2 + 200 \text{ ppm CO})$) was measured again at current densities of 0 to 500 mA cm^{−2} (Eq. (4)). The voltage increase observed for the CO-added hydrogen was more pronounced than that observed when pure hydrogen was used. This was because the HOR overpotential at the Pt–Ru/C catalyst increased due to CO adsorption and decrease in active surface area for the electrochemical reaction.

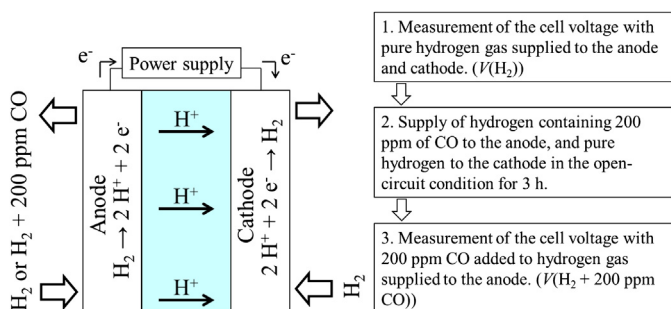


Fig. 1. A schematic diagram of the test cell for evaluation of CO tolerance of the anode.

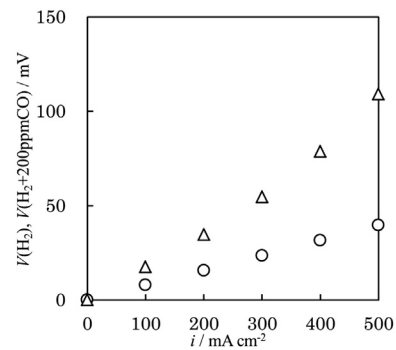


Fig. 2. The voltage required for the hydrogen pump operation. (○): H_2 was supplied to both the anode and cathode. (△): ($\text{H}_2 + 200 \text{ ppm CO}$) was supplied to the anode and H_2 to the cathode.

The difference ($\Delta\eta_a$) in the voltages between the pure hydrogen supply and the CO-added hydrogen supply is used as an indicator for the CO tolerance of the anode (Eq. (5)). The CO tolerance is low when $\Delta\eta_a$ is large.

$$V(\text{H}_2 + 200 \text{ ppm CO}) = \eta_a(\text{H}_2 + 200 \text{ ppm CO}) + \eta_c(\text{H}^+) + IR \quad (4)$$

$$\Delta\eta_a = V(\text{H}_2 + 200 \text{ ppm CO}) - V(\text{H}_2) = \eta_a(\text{H}_2 + 200 \text{ ppm CO}) - \eta_a(\text{H}_2) \quad (5)$$

2.2. Accelerated tests for anode degradation

Hydrogen with high CO content was supplied to the anode to investigate the effect of CO and oxygen on the anode degradation under the accelerated conditions. All the tests were performed at 70 °C under full humidification. First, the CO tolerance was measured in the same manner as described above. Then, hydrogen with a high concentration of CO was supplied to the anode and air was supplied to the cathode in the open-circuit condition for 110 h. The open-circuit voltage fell by a value in the range of 0.9 to 1 V during the accelerated tests. After that, the adsorbed CO on the anode catalyst was removed by an anodic potential sweep. The potential sweeps were performed twice at a scan rate of 0.1 V s^{−1} between 0 and 1 V vs. RHE, while supplying hydrogen to the cathode and nitrogen to the anode. Finally, the CO tolerance of the anode was measured again by the method described above. Then, the difference between the initial CO tolerance and that after the accelerated test was evaluated.

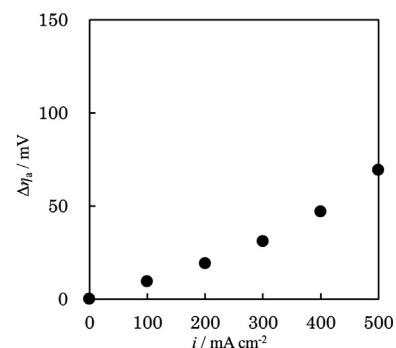


Fig. 3. $\Delta\eta_a$ obtained by Eq. (5) and the data in Fig. 2.

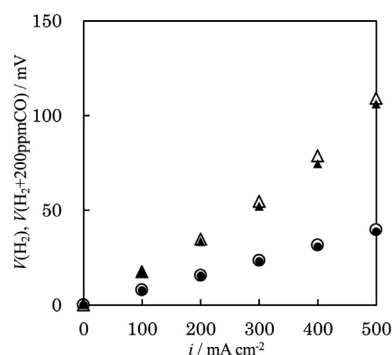


Fig. 4. The voltage required for the hydrogen pump operation before and after the accelerated test with pure hydrogen is supplied to the anode and air is supplied to the cathode. (○): Initial $V(\text{H}_2)$, and (●): $V(\text{H}_2)$ after the accelerated tests. (△): Initial $V(\text{H}_2 + 200 \text{ ppm CO})$, and (▲): $V(\text{H}_2 + 200 \text{ ppm CO})$ after the accelerated tests.

2.3. Measurement of fluoride ion emission

The amount of fluoride ion in the drain water was measured with the aid of ion chromatography (ICS-1500, Dionex Corporation) to evaluate the degradation of the ionomer, which was composed of perfluorocarbon. In this measurement, a hydrocarbon membrane with thickness of 30 μm was used as a membrane electrolyte to avoid the influence of the fluoride ion eluted from the perfluorocarbon membrane.

3. Results and discussion

3.1. Evaluation of CO tolerance

Fig. 2 shows the cell voltages when pure hydrogen is supplied to both the anode and cathode, $V(\text{H}_2)$, and when hydrogen containing 200 ppm of CO is supplied to the anode and pure hydrogen is supplied to the cathode, $V(\text{H}_2 + 200 \text{ ppm CO})$. $V(\text{H}_2 + 200 \text{ ppm CO})$ was larger than $V(\text{H}_2)$, because CO adsorption on the catalyst decreased the active area for HOR. Fig. 3 shows the difference between the $V(\text{H}_2)$ and $V(\text{H}_2 + 200 \text{ ppm CO})$, which is used as the measure of CO tolerance of the anode.

The effect of CO content on the degradation of the anode was investigated by the accelerated cell tests. First, as a control experiment, $V(\text{H}_2)$ and $V(\text{H}_2 + 200 \text{ ppm CO})$ were measured before and after supplying pure hydrogen to the anode and air to the cathode for 110 h under an open-circuit condition. As shown in Fig. 4, $V(\text{H}_2)$

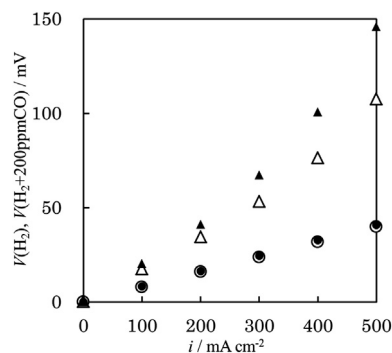


Fig. 5. The voltage required for the hydrogen pump operation before and after the accelerated test with $\text{H}_2 + 500 \text{ ppm CO}$ supplied to the anode and air supplied to the cathode. (○): Initial $V(\text{H}_2)$, and (●): $V(\text{H}_2)$ after the accelerated tests. (△): Initial $V(\text{H}_2 + 200 \text{ ppm CO})$, and (▲): $V(\text{H}_2 + 200 \text{ ppm CO})$ after the accelerated tests.

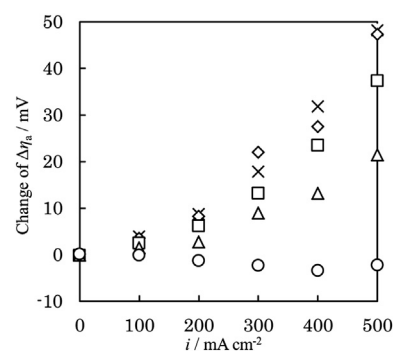


Fig. 6. Changes in $\Delta\eta_a$ after the accelerated tests with hydrogen containing various concentrations of CO supplied to the anode and air supplied to cathode. (○): Pure hydrogen, and (△): hydrogen containing 200 ppm of CO, (□): 500 ppm of CO, (◇): 1000 ppm of CO, (×): 1500 ppm of CO.

and $V(\text{H}_2 + 200 \text{ ppm CO})$ values after the operation (filled circles and filled triangles) were the same as the corresponding values during the operation (open circles and open triangles). However, as seen in Fig. 5, $V(\text{H}_2 + 200 \text{ ppm CO})$ increased after the accelerated tests when hydrogen containing 500 ppm of CO was supplied to the anode for 110 h. Similar measurements were performed by changing CO concentrations to 200 ppm, 1000 ppm, and 1500 ppm during the operation. Fig. 6 shows the changes in $\Delta\eta_a$ after the accelerated tests with various CO concentrations. The CO tolerance was significantly reduced by supplying anode gas with higher concentrations of CO, indicating that CO caused the degradation of the anode during the operation.

The effect of oxygen permeated from the cathode on the degradation of anode was investigated by changing the cathode gas from air to nitrogen. Fig. 7 shows the changes in CO tolerance after the accelerated tests when air (open circles) supplied to the cathode and when nitrogen supplied to the cathode with maintaining the cell voltage at 0.95 V (open triangles). In both the experiments, hydrogen with 1000 ppm of CO was supplied to the anode. The CO tolerance did not change when nitrogen was supplied to the cathode, indicating that the permeation of oxygen through the membrane from the cathode is an essential condition for the degradation of the anode. It is speculated that ORR on the anode catalyst occurs, which generates hydrogen peroxide (H_2O_2) as a by-product. It is well known that H_2O_2 and its derivative, the hydroxyl radical ($\text{OH}\cdot$), decompose the perfluorocarbon membrane electrolytes [9–11]. Thus, the ionomer, composed of perfluorocarbon, is considered to be decomposed by H_2O_2 and $\text{OH}\cdot$, which cause a reduction in the CO tolerance.

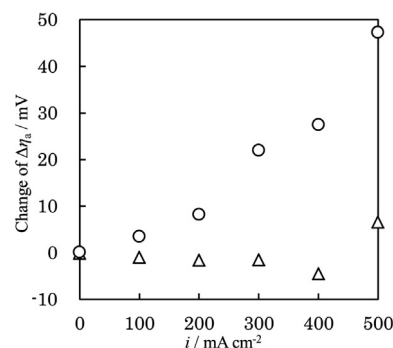


Fig. 7. Changes in $\Delta\eta_a$ after the accelerated tests. (○): The accelerated test with hydrogen containing 1000 ppm CO supplied to the anode and air supplied to the cathode in open-circuit. (△): Nitrogen supplied to the cathode while maintaining the cell voltage at 0.95 V.

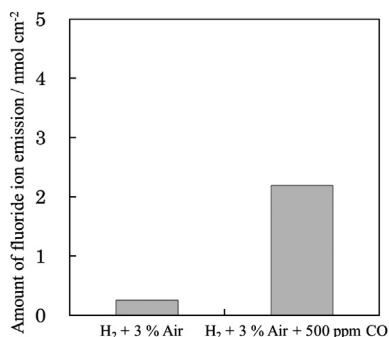


Fig. 8. Amount of fluoride ions in the drain water of the cell. Cell temperature: 70 °C, Anode dew point: 50 °C, Cathode dew point: 50 °C, Cathode gas: Nitrogen.

3.2. Evaluation of fluoride ion emission

Fig. 8 shows the amount of fluoride ion in the drain water of the cell when supplying different gases to the anode and nitrogen to the cathode. When hydrogen containing 3 vol% of air and 500 ppm of CO was supplied to the anode, more number of fluoride ions were emitted compared with the case in which hydrogen containing only 3 vol% of air was supplied. As stated in the previous section, the combination of oxygen and CO is considered to accelerate the degradation of ionomer. In this proposed mechanism, CO is adsorbed on the Pt–Ru alloy catalyst in the anode, thus decreasing the active surface area for electrochemical reaction. Since a small amount of oxygen is permeated through the membrane from the cathode to the anode, ORR is considered to occur on the Pt–Ru alloy catalyst. Then, H₂O₂, which is produced as a by-product, cannot be completely reduced to water because the active surface area of catalyst has been decreased. The produced H₂O₂ degrades the ionomer, which results in degradation decrease in the CO tolerance.

4. Conclusion

The effects of CO and oxygen on the degradation of CO tolerance of a PEFC anode were investigated. When higher concentrations of CO were supplied to the anode during the accelerated tests, the CO tolerances of the anode decreased more significantly. In addition, the CO tolerance did not change when nitrogen was supplied to the cathode, indicating oxygen is an essential for the degradation of the anode. It was also indicated that H₂O₂, a by-product of the ORR at the anode, attacked the perfluorocarbon ionomer in the anode. This was confirmed by the measurement of fluoride ion emission from the cell. The ionomer degradation in the anode is considered to be one of the primary causes for the deterioration of the CO tolerance of the anode.

Acknowledgements

Parts of this study were supported by the New Energy and Industrial Technology Development Organization (NEDO).

References

- [1] R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J.E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. Kimijima, N. Iwashita, *Chem. Rev.* 107 (2007) 3904–3951.
- [2] S.J. Lee, S. Mukerjee, E.A. Ticianelli, J. McBreen, *Electrochim. Acta* 44 (1999) 3283–3293.
- [3] G. Bender, M. Angelo, K. Bethune, R. Rocheleau, J. Power Sources 228 (2013) 159–169.
- [4] J. Zhang, T. Thampan, R. Datta, *J. Electrochem. Soc.* 149 (2002) A765–A772.
- [5] H. Uchida, K. Izumi, M. Watanabe, *J. Phys. Chem. B* 110 (2006) 21924–21930.
- [6] H.A. Gasteiger, N.M. Marković, P.N. Ross Jr., *J. Phys. Chem.* 99 (1995) 16757–16767.
- [7] P.N. Ross, K. Kinoshita, A.J. Scarpellino, P. Stonehart, *J. Electroanal. Chem.* 63 (1975) 97–110.
- [8] M. Inaba, *ECS Trans.* 25 (2009) 573–581.
- [9] T. Kinumoto, M. Inaba, Y. Nakayama, K. Ogata, R. Umebayashi, A. Tasaka, Y. Iriyama, T. Abe, Z. Ogumi, *J. Power Sources* 158 (2006) 1222–1228.
- [10] M. Inaba, H. Yamada, J. Tokunaga, A. Tasaka, *Electrochem. Solid-State Lett.* 7 (2004) A474–A476.
- [11] W. Liu, D. Zuckerbrod, *J. Electrochem. Soc.* 152 (2005) A1165–A1170.